

The Structure and Unusual Hydration/Dehydration Behavior of the New Aluminophosphate SSZ-51

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The aluminophosphate SSZ-51 is a novel molecular "sieve" prepared using 4-(dimethylamino) pyridine as a structure-directing agent in aluminophosphate gels containing fluoride. We studied the calcination and dehydration behaviors of SSZ-51 using powder x-ray diffraction at beamline X7A. We found that the as-made structure changes only slightly when heated to 300°C. However, at 400°C, there are dramatic changes in both the peak diffraction positions and intensities as the organic structure-directing agent and the fluoride are removed from the structure. As water is adsorbed, reversible structural changes occur within the framework of SSZ-51.

The aluminophosphate mineral SSZ-51 is a novel molecular "sieve" prepared using 4-(dimethylamino) pyridine as a structure-directing agent in aluminophosphate gels containing fluoride. The SSZ-51 unit cell is monoclinic, with $a = 21.759$, $b = 13.821$, $c = 14.224$ Å, and $\beta = 98.85^\circ$. The structure of SSZ-51 (**Figure 1**) is closely related to the silicoaluminophosphate SAPO-40. Both structures possess intersecting 12- and 8-ring channels.

The powder diffraction pattern of SSZ-51 changes dramatically after calcination, which removes the occluded organic template and fluoride ions (**Figure 2**). Except for the low-angle 110 and 200 peaks, the diffraction pattern of the calcined material shows little resemblance to the as-made form, suggesting perhaps that the material is decomposing during calcination. However, it was quite puzzling that SSZ-51 possessed an appreciable microporosity, and that adsorption measurements were consistent with the presence of 12- and 8-rings in the calcined structure. We therefore decided to collect variable temperature powder diffraction data at beamline X7A on the as-made sample, to monitor structural changes as SSZ-51 was heated in air.

The sample was placed in a glass capillary and heated in open air in 100°C increments up to 800°C. After completing the initial series of experiments to remove the organic component, the material was placed over a beaker containing water. After hydrating for a day, the sample was loaded into another capillary and data were again collected in 100°C increments.



Figure 3 shows the effect of temperature on the powder diffraction pattern of the as-made sample of SSZ-51. As the material is heated to 300°C, there are only slight changes in the x-ray

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diffraction (XRD) pattern. However, at 400°C there are dramatic changes in both the peak positions and intensities as the organic structure-directing agent and the fluoride are removed from the structure. The shifts are readily apparent in the positions of the 110, 200, and 310 reflections. This XRD pattern can be indexed by a C-centered monoclinic cell with lattice parameters of $a = 22.471$, $b = 13.735$, $c = 14.052$, and $\beta = 98.5^\circ$. While the other lattice parameters show little change, the a lattice parameter increases by 3.3%. This change seems mostly due to the relaxation of the framework as the fluoride bonds with the framework are broken.

After 400°C, there is little variation in the pattern. At 800°C the XRD pattern shows some disparity near 9.43 and 11.98 $^\circ 2\theta$, likely due to structural changes in the berlinite impurity, which exhibits a phase transition near 600°C.

We were surprised that the material survived calcination to 800°C. We then thought that the changes we initially observed in the XRD pattern might be due to adsorption of water rather than to thermal instability. If we allowed the sample to hydrate for a day, would we then obtain the grotesque XRD pattern we observed in our calcined samples? If so, could we reheat the sample and recover a nice “crystalline” diffraction pattern? **Figure 4** shows that the answer to both questions is “Yes.” In fact, at 100°C, most of the expected reflections from the unit cell are distinctly visible.

So how do we explain these reversible structural changes induced by water? It appears the adsorbed water removes the long-range order from the otherwise crystalline structure. Water is known to coordinate with aluminum atoms in the frameworks of aluminophosphate zeotypes to produce octahedrally coordinated aluminum species. In some cases water may even hydrolyze the framework bonds to destroy the structure. If the water molecules do not bond to each crystallographically equivalent aluminum atom in the same manner, the long-range symmetry of the structure is lost and a diffraction pattern is obtained with features similar to the one at the bottom of **Figure 2**.

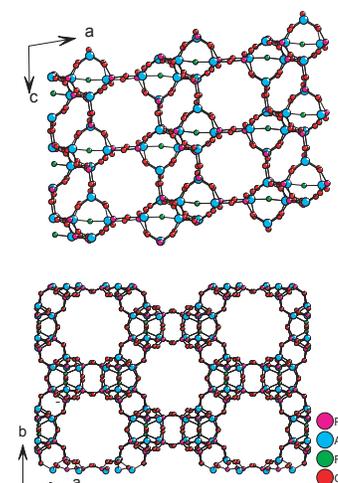


Figure 1. Structure of the novel aluminophosphate SSZ-51.

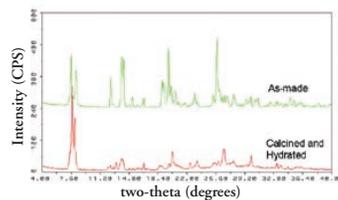


Figure 2. XRD (CuK α) patterns of SSZ-51 taken before and after calcination.

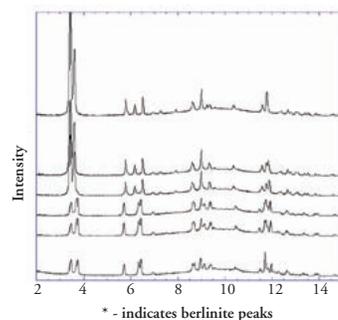


Figure 3. Calcination of the as-made form of SSZ-51.

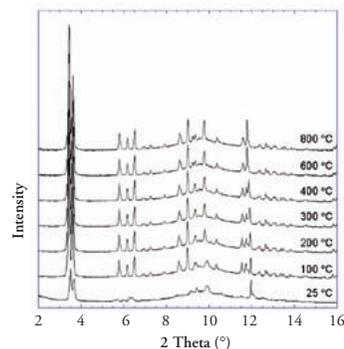


Figure 4. Dehydration of calcined SSZ-51.